POLYPHENYLQUINOXALINES CONTAINING ALKYLENEDIOXY GROUPS

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Synopsis

A series of new polyphenylquinoxalines (PPQ) containing alkylenedioxy units within the backbone were prepared in high molecular weight forms (η_{inh} = 0.82-1.5 dL/g). The glass transition temperatures ranged between 203 and 241°C, decreasing with increasing length of the alkylenedioxy groups. Solution cast films gave tensile strength, tensile modulus and elongation at room temperature as high as 14,400 psi, 378,000 psi and 8.1%, respectively. The PPQ were readily compression molded to provide compact tension specimens that gave fracture energy (G_{Ic}) as high as 10.5 in-lb/in^2. Titanium to titanium tensile shear specimens provided average strengths of 4400 psi at 26°C, 3100 psi at 177°C, and 2010 psi at 203°C. The PPQ were resistant to normal aircraft fluids but were soluble in chlorinated solvents.

INTRODUCTION

A variety of structurally different polyphenylquinoxalines (PPQ) have been synthesized for possible use in high temperature applications.[1] These

structures were usually fully aromatic, with the expected high glass transition temperatures and high processing temperatures. For many applications, including adhesives and matrices in composite structures on aerospace vehicles, exceptionally high thermal stability is not always required. Ease of processing and good mechanical properties are often more desirable.

The incorporation of a flexibilizing segment such as an aliphatic or an alkylenedioxy group into the repeat unit of an aromatic/heterocyclic polymer is an effective means of reducing the glass transition temperature and improving the processability. Aliphatic groups have been incorporated within many heterocyclic polymers such as imide,[2] benzimidazole[3] and phenylquinoxaline.[4] Polyimides containing alkylenedioxy units in the main chain have also been reported.[5-7]

To further investigate the use of alkylenedioxy units in heterocyclic polymers, a series of PPQ containing α,ω-alkylenedioxy units of various lengths were synthesized. The physical and mechanical properties of these polymers are reported herein.

EXPERIMENTAL

Starting Materials

Benzyl 4-hydroxyphenyl ketone was either used as purchased from Aldrich Chemical Co. or prepared by the Fries Rearrangement of benzyl benzoate in nitrobenzene[8] (61% yield after recrystallization from toluene, m.p. 144-148°C). The α,ω-dibromoalkanes were purchased from Aldrich Chemical Co. and used as-received. 3,3'-Diaminobenzidine (DAB) was recrystallized twice from water containing a small amount of sodium dithionite to yield

light tan crystals, m.p. 174-176°C (lit[9] m.p. 179-180°C). m-Cresol was distilled under nitrogen at reduced pressure before use.

Monomer Synthesis

4,4'-Bis(phenylacetyl)-α,ω-diphenoxyalkanes

The synthesis of a series of 4,4'-bis-(phenylacetyl)-α,ω-diphenoxyalkanes(1a-e) was accomplished by the reaction of benzyl 4-hydroxyphenyl ketone with the appropriate α,ω-dibromoalkane in the presence of potassium carbonate (Eq. 1). The synthesis of 4,4'-bis(phenylacetyl)-1,4-diphenoxybutane (1c) will serve as a typical example. Benzyl 4-hydroxyphenyl ketone (10.66 g, 0.050 mol) and 1,4-dibromobutane (5.40 g, 0.025 mol) were dissolved in 30 mL of N,N-dimethylformamide (DMF). Powdered anhydrous potassium carbonate (8.64 g, 0.0625 mol) was added and the stirred mixture maintained at 130-140°C for 4 h under a nitrogen atmosphere. The reaction mixture was allowed to cool slightly, then added to water to precipitate a gummy solid. The solid was collected by filtration, dried, stirred with methanol, and filtered to remove unreacted 1,4-dibromobutane. The 10.6 g of crude solid was recrystallized from ca. 200 mL of toluene to provide 1c (9.37 g, 78%); m.p. 170.5-171.5°C; IR (KBr) 1677 cm^{-1} (vs, sharp, C=O); ^1H NMR spectra was not obtained as 1a-e were not soluble in any common solvent at room temperature. Anal. Calcd for $C_{32}H_{30}O_4$: C, 80.31; H, 6.32 Found: C, 80.03; H, 6.56. Melting points, yields after recrystallization from toluene, and elemental analyses of 1a-e are given in Table 1.

4,4'-(α,ω-Diphenoxyalkane) bis(phenylethanediones)

The corresponding 4,4'-(α,ω-diphenoxyalkane) bis(phenylethanediones) 2a-e were obtained by the selenium dioxide oxidation of 1a-e in refluxing glacial acetic acid (Eq. 1). The synthesis of 4,4'-(1,4-diphenoxybutane)

bis(phenylethanedione) (2c) will serve as a typical example. 4,4'-Bis-(phenylacetyl)-1,4-diphenoxybutane (17.23 g, 0.036 mol) and selenium dioxide (7.99 g, 0.072 mol) were stirred at reflux for 4 h in 100 mL of glacial acetic acid. The hot mixture was filtered in order to remove the black suspension of selenium metal. The filtrate was allowed to cool, and the crystallized yellow solid collected by filtration and dried to provide 14.6 g of crude solid. Recrystallization from ca. 200 mL of toluene afforded 2c (13.18 g, 72%) as a light yellow solid; m.p. 150.5-152°C; IR (KBr) 1670, 1665, and 1659 cm^{-1} (s, C=O); ^1H NMR (DMF-d_7) δ 1.8-2.2 (m, 4H, CH_2), 4.23 (t, 4H, $ArOCH_2$, J=4.5 Hz), 7.0-8.15 (m, 18 H, aromatic). Anal. Calcd for $C_{32}H_{26}O_6$: C, 75.88; H, 5.17. Found: C, 75.90; H, 5.32. Melting points, yields after recrystallization from toluene, and elemental analyses of 2a-e are given in Table 2.

Polymer Synthesis

The polyphenylquinoxalines (PPQ, 3a-e) were synthesized by the polymerization of a stoichiometric amount of the appropriate bis(α-diketone) (2a-e) with 3,3'-diaminobenzidine (DAB) in m-cresol (ca. 12% solids concentration by weight). Specifically, 4,4'-(1,4-diphenoxybutane) bis(phenylethanedione) (10.1310 g, 0.0200 mol) was dissolved in 100 mL of m-cresol (warming) under a nitrogen atmosphere and the solution was allowed to cool to room temperature. 3,3'-Diaminobenzidine (4.2854 g, 0.0200 mol) was added to the solution and the mixture stirred at room temperature for 4 h, followed by heating at 120-140°C for 2 h. The PPQ was isolated by precipitation of the viscous solution in methanol. The PPQ was collected by filtration, boiled in methanol, filtered and subsequently dried under vacuum at 200°C.

Yields were essentially quantitative. Characterization of the PPQ is shown in Table 3.

Films

Chloroform/m-cresol solutions (~14% solids content) of the polymers were centrifuged, the decantate doctored onto plate glass and dried at ~45°C to a tack-free form in a dust-proof chamber. The films on glass were further stage-dried to a temperature of 100°C in air and 200°C *in vacuo*. The 2.5 mil thick transparent yellow films were tested according to ASTM D882 using four to six specimens per test condition.

Molded Specimens

In a 1.25 in. square stainless steel mold, polymers were compression molded at 300-320°C under 150 psi. Miniature compact tension specimens were cut from the moldings and subsequently tested to determine fracture toughness according to ASTM E399 using four specimens per polymer.

Adhesive Specimens

Titanium to titanium tensile shear specimens with a Pasa-Jell 107 surface treatment were fabricated by increasing the temperature from 26°C to 316°C under 200 psi during ~45 min and holding at 316°C under 200 psi for 0.5 hr. The adhesive tape was prepared by multiple solution coating of 112-A1100 E glass and subsequently dried after each coat. The final volatile content was < 1%. Four specimens per test condition were pulled according to ASTM D1002.

Characterization

Melting points were determined by using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared (IR) spectra were obtained on a Perkin-Elmer Model 297 spectrophotometer. Proton nuclear

magnetic resonance (^{1}H NMR) spectra were taken on a Varian EM 360A spectrometer with tetramethylsilane as internal standard. Inherent viscosities were obtained from 0.5% solutions in chloroform at 25°C. Elemental analysis was performed by Galbraith Laboratories, Inc., Knoxville, TN. Differential scanning calorimetry (DSC) was performed at a heating rate of 20°C/min with the glass transition temperature (Tg) taken at the inflection point of the ΔT versus temperature curve. Samples were heated to a temperature ~40°C above the Tg, quenched and rerun. Torsional braid analysis (TBA) was conducted at a heating and cooling rate of 3°C/min with the Tg taken as the temperature of the damping peak during the cool-down after heating to 300°C in nitrogen. Thermal mechanical analysis (TMA) of films in the elongation mode was performed at a heating rate of 5°C/min with 2 g added weight using the DuPont Model 940 module. Thermogravimetric analysis (TGA) was conducted at a heating rate of 2.5°C/min in flowing air or nitrogen on powder samples.

RESULTS AND DISCUSSION

Monomer Synthesis

A few unsuccessful routes to synthesize the 4,4'-bis(phenylacetyl)-α,ω-diphenoxyalkanes (1a-e) were attempted. For example the reaction of 1-(4-fluorophenyl)-2-phenylethanone with 1,4-butanediol in the presence of potassium carbonate was unsuccessful. A model reaction using sodium ethoxide in place of 1,4-butanediol in refluxing N,N-dimethylacetamide in the presence of a catalytic amount of copper also failed to yield the desired product. Another approach involved the Friedel-Crafts acylation of

1,2-diphenoxyethane with phenylacetyl chloride. The reaction proceeded readily at 10-15°C in either methylene chloride or carbon disulfide, but the product contained a mixture of isomers. After two recrystallizations from toluene, the product was found by high pressure liquid chromatography (HPLC) analysis to contain 93% of 1a. The remainder was apparently ortho-substituted isomers.

The reaction of benzyl 4-hydroxyphenyl ketone with the appropriate α,ω-dibromoalkane in the presence of potassium carbonate (Eq. 1) provided 1b-e in good yields (Table 1). The poor yield of 4,4'-bis(phenylacetyl)-1,2-diphenoxyethane (1a) probably resulted from the competing elimination reaction of ethylene dibromide in the alkaline reaction mixture. Oxidation of 1a-e with selenium dioxide to the corresponding bis(α-diketones) (2a-e) went smoothly (Table 1). The lower yield for 4,4'-(1,2-diphenoxyethane) bis(phenylethanedione) (2a) was due to loss of material during workup and not to incomplete oxidation.

Polyphenylquinoxaline (PPQ) Synthesis and Characterization

Polymerization of the bis(α-diketones) (2a-e) with 3,3'-diaminobenzidine (DAB) in m-cresol proceeded readily to form extremely viscous solutions. The polymers were precipitated in methanol and dried to yield fluffy yellow solids with inherent viscosities from 0.82 to 1.50 dL/g (Table 3). The polymers were readily soluble in chlorinated solvents such as chloroform and sym-tetrachloroethane. However, film specimens under stress (by bending 0.8 in long x 0.25 in wide x 0.0025 in. thick strips back upon themselves) were unaffected after immersion for 72 hr in ethylene glycol (deicing fluid), JP-4 jet fuel, and tricresyl phosphate (hydraulic fluid).

The glass transition temperatures of PPQ were determined by three different methods and are reported in Table 3. Although the actual values differ by as much as 10 degrees from one method to another, the trend is the same. As the length of the alkylenedioxy unit increases, the Tg decreases. By DSC, the PPQ containing an ethylenedioxy unit had a Tg of 241°C and the PPQ containing a 1,6-hexylenedioxy group exhibited a Tg of 203°C.

By TGA, the α,ω-alkylenedioxy containing PPQ displayed initial weight loss at temperatures lower than expected. For example, the butylenedioxy containing PPQ (3c) exhibited initial weight loss at ~380°C with a 5% weight loss at 440°C in nitrogen (Figure 1). In air, the same PPQ exhibited initial weight loss at ~320°C and 5% weight loss at 420°C.

Thin film properties of PPQ (3b-e) are reported in Table 4. The tensile strength and modulus of 3b and 3c (propylenedioxy and butylenedioxy containing PPQ) were higher than the polymers with longer alkylenedioxy units (3d and 3e). However the latter polymers, being more flexible, gave slightly higher elongations as expected. In general, the thin film properties were relatively good with high retention of properties at 93°C. For comparison, thin film properties of an all-aromatic PPQ (from 4,4'-oxydibenzil and DAB) were tensile strength of 17,000 psi, tensile modulus of 400,000 and elongation of 23% at 26°C.

Despite Tgs of 203-241°C, the PPQ were easily compression molded at 300-320°C under 150 psi. The fracture toughness or critical strain energy release rate (G_{Ic}) were obtained on miniature compact tension specimens with precracks introduced via a cold razor blade. The α,ω-alkylenedioxy containing PPQ, polymers 3b, 3c, 3d and 3e, gave G_{Ic} of 5.4, 8.3, 10.5 and 10.5 in-lb/in^2 respectively. The G_{Ic} increased as the length of the

alkylenedioxy group increased. For comparison, the G_{Ic} of a PPO (from 4,4'-oxydibenzil and DAB), Union Carbide's polysulfone (UDEL® P-1700), and General Electric's polyetherimide (Ultem® 1000) were 14.6, 18.3 and 21.1 in.-lb/in^2 respectively.

Average Ti to Ti tensile shear strengths for 1,4-butylenedioxy containing PPO (3c) were 4400 psi at 26°C, 4200 psi at 93°C, 3900 psi at 150°C, 3100 psi @ 177°C and 2010 psi at 203°C. The failures were predominantly cohesive.

CONCLUSIONS

Polyphenylquinoxalines containing alkylenedioxy groups of 2 to 6 carbon atoms were prepared in high molecular weight forms with Tgs of 203 to 241°C. Thin films and Ti/Ti adhesive specimens gave good mechanical properties. The polymers were readily compression molded to provide compact tension specimens which exhibited G_{Ic} as high as 10.5 in.-lb/in^2. By TGA, a polymer exhibited 5% weight loss in air and in nitrogen at 420 and 440°C respectively.

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TABLE 1

Physical Constants of 4,4'-Bis(phenylacetyl)-α,ω-diphenoxyalkanes

Compd (see Eq. 1)	m.p., °C	Yield[a] (%)	Elemental Anal. Calc. C, %	Calc. H, %	Found C, %	Found H, %
1a	184.5-186.5	13	79.98	5.82	79.87	6.01
1b	137.5-139	67	80.15	6.07	80.05	6.17
1c	170.5-171.5	78	80.31	6.32	80.03	6.56
1d	108.5-109.5	68	80.46	6.55	80.84	6.81
1e	153-156	86	80.60	6.76	79.89	6.92

[a]Yield after recrystallization from toluene.

TABLE 2

Physical Constants of 4,4'-(α,ω-Diphenoxyalkane) bis(phenylethanediones)

Compd (see Eq. 1)	m.p., °C	Yield[a] (%)	Elemental Anal. Calc. C, %	Calc. H, %	Found C, %	Found H, %
2a	170-173	45	75.30	4.63	75.64	4.86
2b	190.5-191.5	72	75.60	4.91	75.32	5.06
2c	150.5-152	72	75.88	5.17	75.90	5.32
2d	143.5-145	79	76.14	5.42	76.22	5.65
2e	132.5-133.5	77	76.39	5.66	76.35	5.88

[a]Yield after recrystallization from toluene.

TABLE 3

Characterization of Polyphenylquinoxalines

PPQ (see Eq. 2)	η_{inh}[a] (dL/g)	DSC[b]	Tg (°C) TBA[c]		TMA[d]
			Heat-up	Cool-down	
3a	0.82	241	236	249	238
3b	1.05	238	232	243	237
3c	0.93	220	219	225	230
3d	1.14	212	203	214	218
3e	1.50	203	197	203	212

[a]Inherent viscosity, 0.5% solution in chloroform at 25°C.

[b]Differential scanning calorimetry at heating rate of 20°C/min.

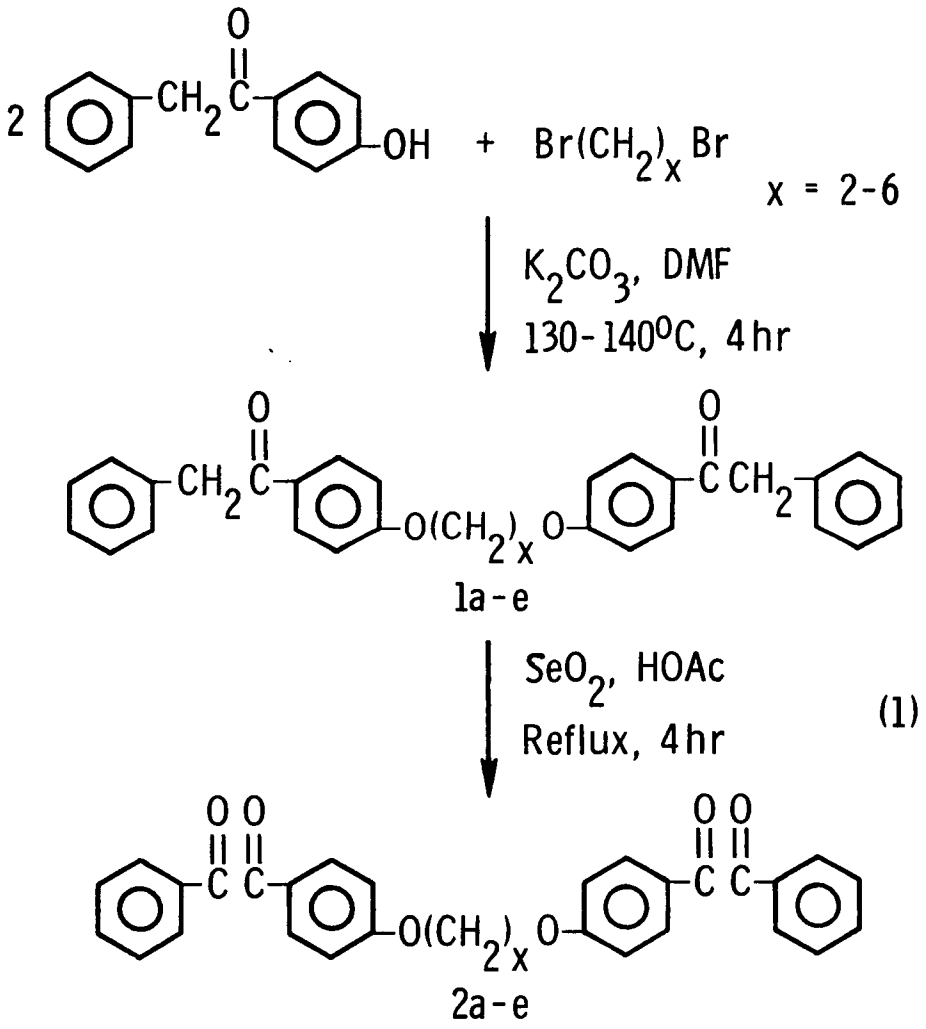
[c]Torsional braid analysis at heating rate of 3°C/min.

[d]Thermal mechanical analysis at heating rate of 5°C/min.

TABLE 4

Thin Film Properties of Polyphenylquinoxalines

PPQ (see Eq. 2)	Tensile Yield (10^3 psi)		Tensile Strength at Break (10^3 psi)		Tensile Modulus (10^5 psi)		Elongation at Break (%)	
	RT	93°C	RT	93°C	RT	93°C	RT	93°C
3b	7.1	6.7	14.3	10.6	3.74	2.98	7.3	5.6
3c	7.3	7.2	14.4	10.8	3.78	2.92	8.1	10.5
3d	7.3	6.5	12.9	9.8	2.85	2.54	10.7	47.6
3e	7.3	6.4	12.7	9.3	3.08	2.48	10.7	12.5


2
CH2
C
O
OH
+ Br(CH2)x Br
x = 2-6
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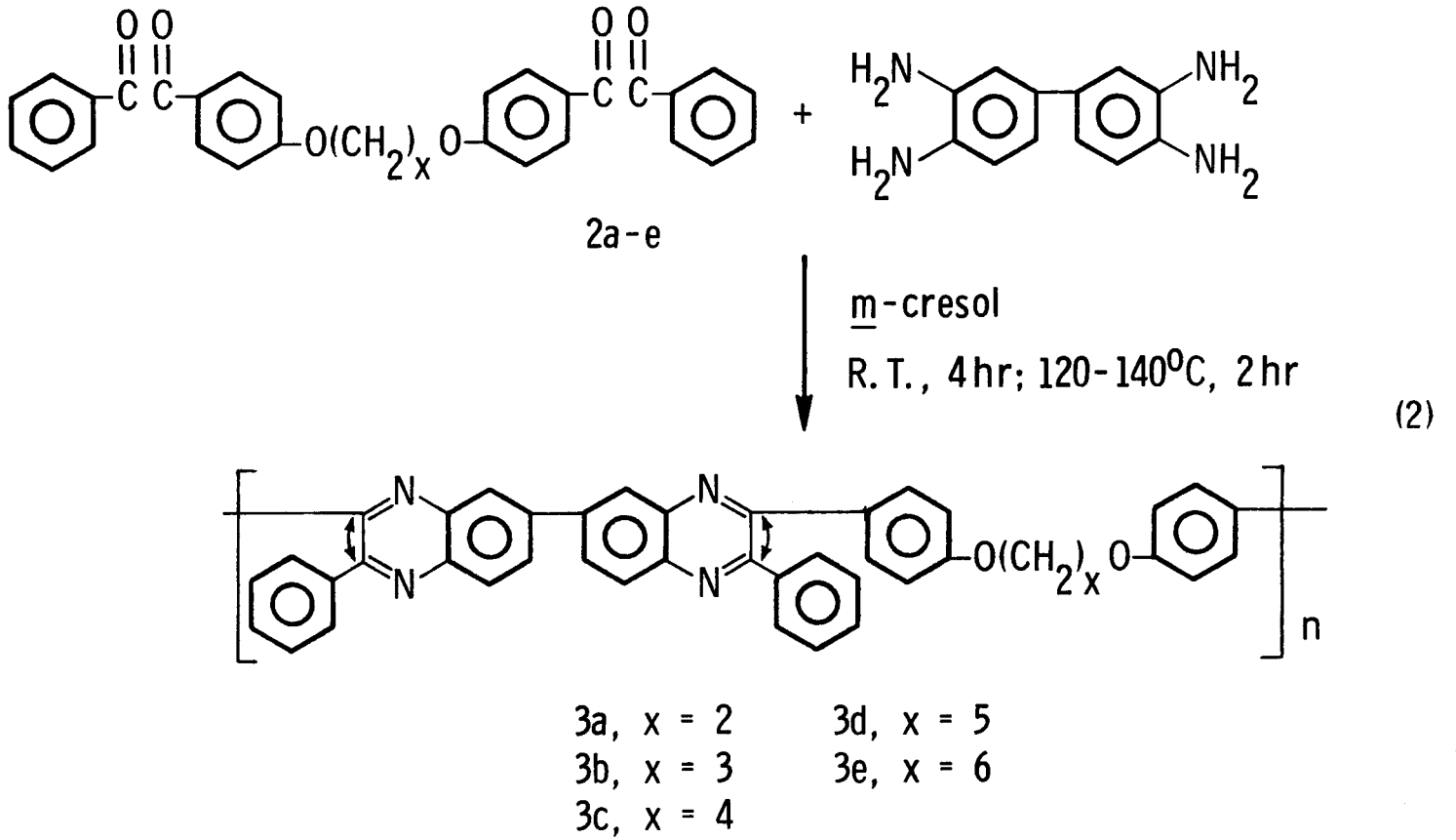
130-140°C, 4hr
O(CH2)x O
1a-e
SeO2, HOAc
Reflux, 4hr
2a-e

(1)



(2)

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3b, x = 3
3c, x = 4
3d, x = 5
3e, x = 6

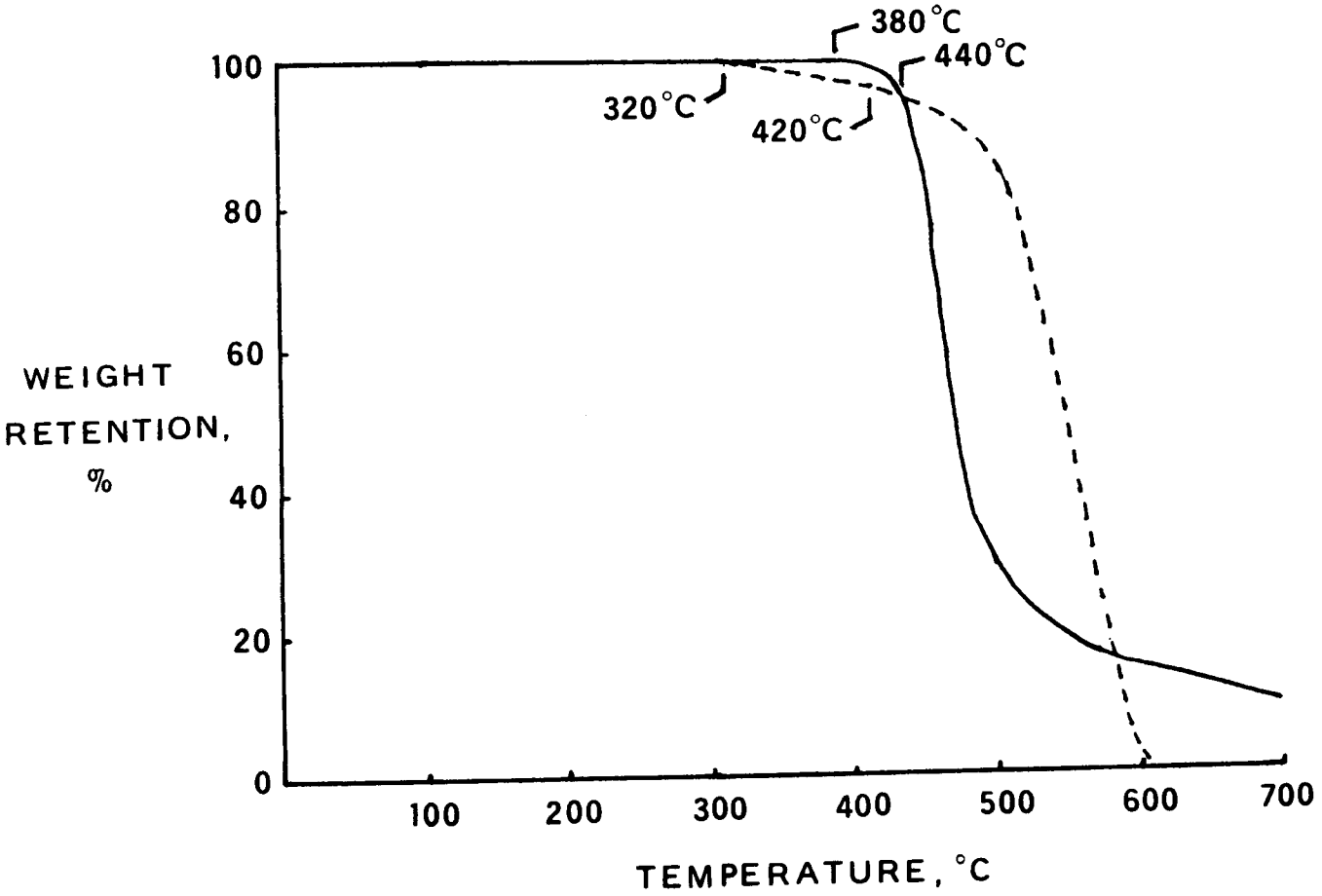

Fig. 1. Thermogravimetric analysis curves of PPQ (3c) in nitrogen (—) and flowing air (---). Heating rate: 2.5°C/min; sample form: powder.